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Estimation of Tetryl, alone or in Mixtures with T.N.T., by Ferrous Ammonium Sulphate

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COPE and Barab[1] have shown that the nitroamino group in tetryl and certain other nitroamines, such as nitro-urea and nitro-guanidine, is quantitatively converted into nitric oxide in the nitrometer; the volume of nitric oxide is thus a possible measure of tetryl. Another method,[2] less specific and confined to its estimation in mixtures with T.N.T., makes use of the relative insolubility of tetryl in carbon tetrachloride. In this method, due to Taylor and Rinkenbach,[2] rigorous conditions have been prescribed; but even following these conditions the authors admit an error of 2% for the method, the error increasing with the percentage of T.N.T. present in the mixture.

The nitrometer method of estimating tetryl has been developed by Lehmstedt.[3] According to him, the method is both rapid and accurate; applied to a 1 : 1 mixture of tetryl and T.N.T., it gave values of 49·8, 49·5 and 49·7%, and it does not affect tetranitroaniline.

Desvergnes[4] finds that the estimation of tetryl in the nitrometer has limitations; *e.g.*, tetryl is not easily soluble in the restricted volume of conc. sulphuric acid used, nor is it easy to get the mixture into the nitrometer quantitatively. Desvergnes raises, however, another objection which is difficult to understand, namely, that it takes a long time (about 4 hr.) to complete the liberation of NO. He has no doubt that the dissolution of tetryl in sulphuric acid could be hastened by warming, but not without decomposition and consequent low values.

There would thus appear to be no established method for the accurate estimation of tetryl. We therefore began with an examination of the nitrometer method. Although we could not substantiate in their entirety the criticisms of this method by Desvergnes, our own experience of the method is that it is cumbersome; the dissolution of tetryl in the small quantity of sulphuric acid fixed by the working conditions of the nitrometer is not only time-consuming but unsatisfactory. Working with pure tetryl, it was difficult to get a value more than 97% by the nitrometer.

It thus became clear that there is a real need to estimate the nitric acid released from tetryl on dissolution in sulphuric acid, by a method less strenuous than the nitrometer method. The estimation of nitric acid by titration against ferrous ammonium sulphate suggested itself. Preliminary trials showed that this titration has the very great advantage over gas measurement, that there is no limit to the volume of sulphuric acid to be used, obviating the main difficulty of dissolving tetryl and insuring the quantitative release of nitric acid.

METHOD—About 0·75 g of finely ground tetryl (100 B.S. mesh) is accurately weighed into a 350-ml conical flask, 100–120 ml of ice-cold conc. sulphuric acid are added and the flask is stoppered. The mixture is kept at ice temperature until dissolution is complete and then titrated against ferrous ammonium sulphate as described by Mitra and Srinivasan[5] in the estimation of guncotton. The standardised ferrous solution (note iii) is run in very slowly, with continuous mixing, through a fine jet attached to the burette, the end being well below the surface of the acid. Mixing must be very thorough in order to avoid local concentrations of $Fe^{\cdot\cdot}$ which may cause a precipitate to form, vitiating the results. Near completion, the standard should be added, drop by drop. The end-point is indicated by a permanent pink colour. ($FeSO_4$: NO complex.)

Notes: (i) The tetryl should be finely subdivided to help dissolution.

(ii) Temperature of dissolution and titration should not exceed 0° C. Strict adherence to this low temperature is very necessary, not so much to prevent loss of nitric acid (the normal precaution in these titrations) as to avoid a browning of colour which occurs in varying degrees at laboratory temperatures and masks the end-point. If solution is completed at 0° C. the colour is pale yellow.

(iii) The ferrous ammonium sulphate solution used in this titration (120 g/litre in 60% sulphuric acid wt/vol.) is rather dilute, the concentration fixed being the optimum for the working conditions of the experiment (about 20 ml titre for 0·75 g of tetryl). This dilute solution, in contradistinction to the strong

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solution used in guncotton estimation, shows a tendency to change on keeping. To avoid frequent standardisation of the solution, therefore, it is best preserved in a bottle closed with an automatic burette, the air space being filled with hydrogen. The solution is standardised against potassium nitrate (0·25 g).

Accurate results for pure tetryl are obtained by following the above details (Table I). As nuclear nitro groups are unaffected by sulphuric acid, the method is applicable with equal accuracy to estimation of tetryl in mixtures with T.N.T. (Table II).

The mechanism of the reaction between tetryl and sulphuric acid, about which there is little definite information in the literature, is under investigation.

RESULTS—

TABLE I

Nitroamine nitrogen % in tetryl (theoretical = 4·88)

Found: 4·89; 4·87; 4·83; 4·85; 4·85; 4·91; 4·91; 4·90; 4·85; 4·89; 4·88; 4·91; 4·92

Average 4·88%: Standard deviation 0·091; coeff. of variability 1·9%.

TABLE II

ESTIMATION OF TETRYL IN MIXTURES WITH T.N.T.

Tetryl present:	50·03%	30·03%	80·04%
,, found:	49·84%	29·73%	80·04%
	49·84%	29·70%	80·05%

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